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(19)

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(54) PROCESS FOR THE PRODUCTION OF LIQUEFIED PETROLEUM GAS

(71) We, UNIVERSAL OIL PRODUCTS COMPANY, a corporation organized under the laws of the State of Delaware, United States of America, of No. Ten UOP Plaza, Algonquin & Mt. Prospect Roads, Des Plaines, Illinois, 60016, United States of America, do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following Statement:—

The present invention is directed toward a two-stage hydrocracking process for the direct production of LPG from heavier-than-gasoline hydrocarbon fractions and/or distillates. The phrase "gasoline boiling range hydrocarbons" is intended to connote various hydrocarbon fractions having an end boiling point which ranges from 350°F. to 450°F. To some extent, the precise boiling range for a naphtha fraction depends upon the particular locale in which the same is defined. It is not, therefore, intended to limit the present invention to a particular boiling range when reference is made to gasoline boiling range hydrocarbons. Heavier-than-gasoline charge stocks, contemplated for utilization in the present combination process, will have, therefore, an initial boiling point in the range of 350°F. to 800°F. Thus, suitable charge stocks include kerosene fractions, light gas oils boiling up to a temperature of 700°F., heavy vacuum or atmospheric gas oils boiling up to a temperature of 1050°F. and either intermediate, or overlapping fractions and mixtures thereof. Charge stocks, containing hydrocarbons which normally boil above a temperature of 1050°F. (considered in the art as "black oils") are suitable but will generally require a pretreatment for the purpose of converting the 1050°F.-plus material into lower-boiling hydrocarbons as well as eliminating metallic and asphaltenic contaminants.

The process of the present invention is probably most applicable in those areas which (1) have no virgin source of natural gas and (2) are remote from pipelines transporting the same. Furthermore, within the petroleum industry, it is generally conceded that the demand for natural gas is rapidly exceeding the supply thereof at a rate such that the latter will be exhausted in a period of about seven to about ten years. In many areas, LPG serves as a substitute for natural gas primarily for cooking and heating. A much preferred use for LPG is acknowledged to be as charge stock in a steam-reforming process for the production of a methane-rich "synthetic natural gas", which is often referred to as "town gas".

The present invention seeks to convert heavy hydrocarbonaceous charge stocks boiling above the gasoline boiling range to lower-boiling hydrocarbon products, specifically a propane/butane concentrate (LPG).

According to the invention there is provided a process for the production of liquefied petroleum gas, which process comprises the steps of: (a) reacting a hydrocarbonaceous charge stock boiling above the gasoline boiling range and hydrogen in a first reaction zone at hydrocracking conditions selected to produce gasoline boiling range hydrocarbons; (b) separating the resulting first reaction zone effluent in a first separation zone at substantially the same pressure as in the first reaction zone and at a temperature to provide a first vaporous phase containing gasoline boiling range hydrocarbons and a first liquid phase containing hydrocarbons boiling above the gasoline boiling range; (c) reacting said first vaporous phase in a second reaction zone at hydrocracking conditions selected to convert normally liquid hydrocarbons to liquefied petroleum gas components; (d) separating the resulting second reaction zone effluent in a second separation zone at substantially the same pressure as in the second reaction zone and a temperature in the range of 60°F. to 140°F. to provide a second vaporous phase and a second liquid phase; and, (e) further separating said second liquid phase to provide a third liquid phase containing unreacted

gasoline boiling range hydrocarbons and to recover said liquefied petroleum gas.

Suitably, at least a portion of said third liquid phase is recycled to said second reaction zone.

It is well known that LPG can be produced in relatively high yields from naphthas, or gasoline boiling range hydrocarbons, having end boiling points in the range of 350°F. to 450°F. In most commercial LPG installations, the general practice is to produce a naphtha charge stock with an end boiling point of 380°F. to 410°F. With charge stocks containing extremely heavy components—e.g. those having normal boiling points in the range of 900°F. to 1050°F.—a relatively high severity operation is required to maximize the yields of the LPG propane/butane concentrate. The high severity operation, required to convert such heavy components directly to LPG, produces an adverse effect upon the stability of the catalytic composite employed in the reaction zone. A common practice involves the initial conversion of such heavy hydrocarbonaceous material into a 400°F. end point naphtha through the use of a multiple-stage system, with a naphtha product subsequently being processed in a separate reaction zone for conversion into LPG.

As hereinbefore stated, the present invention involves a multiple-stage hydrocracking system for the direct production of liquefied petroleum gas from hydrocarbon charge stocks boiling above the gasoline boiling range. These heavy charge stocks, for example, a full boiling range gas oil having an initial boiling point of 500°F. and an end boiling point of 1050°F., are generally contaminated through the inclusion of sulfurous and nitrogenous compounds. These charge stocks will, therefore, generally be subjected to a hydrotreating, or hydrorefining technique whereby the deleterious contaminating influences are converted into hydrogen sulfide, ammonia and hydrocarbons. Hydrorefining, or desulfurization reactions are effected at a maximum catalyst bed temperature of 600°F. to 850°F. a pressure in the range of 500 to 5,000 psig., a hydrogen concentration from 1,000 to 20,000 scf./Bbl. and a liquid hourly space velocity of from 0.25 to 10.0. Suitable desulfurization catalysts are thoroughly described in the literature, and only brief reference thereto is necessary therein. Suitable catalytic composites generally comprise a siliceous refractory inorganic oxide carrier material and at least one metallic component selected from the metals and compounds of the metals of Groups VI—B and VIII (iron-group) of the Periodic Table. One commonly employed carrier material is a composite of alumina and from 10.0% to 90.0% by weight of silica. Suitable metallic components include chromium, molybdenum, tungsten, iron, cobalt and nickel. The Group VI-B metal, such as molybdenum, is usually present within the range of 4.0% through 30.0% by weight. The Group VIII metals, such as nickel, is usually present in an amount in the range of 0.01% to 10.0% by weight. In those instances where the catalytic composite is to contain a Group VIII noble metal, the same is generally present in an amount within the range of 0.01% to 2.0% by weight.

With respect to the hydrocracking reaction zones, maximum catalyst bed temperatures will normally be within the range of 650°F. to 950°F. and preferably from 700°F. to 900°F. In most applications of the present invention, the maximum catalyst bed temperature within the second hydrocracking reaction zone will be higher than that in the first hydrocracking reaction zone. The hydrocracking reaction zones are normally maintained under an imposed pressure in the range of 1,000 to 5,000 psig., and preferably from 1,000 to 2,500 psig. The rate of hydrocarbon charge will normally be in the range of 0.25 to 5.0 liquid hourly space velocity, and the hydrogen concentration will be normally in an amount of 3,000 to 30,000 scf/Bbl. The hydrocracking catalytic composites will normally comprise at least one metallic component selected from groups VI-B and VIII of the Periodic Table, rhenium, tin and germanium, and a composite of silica and from 12.0% to 30.0% by weight of alumina. A particularly preferred catalytic composite for utilization in the second hydrocracking reaction zone wherein the greater proportion of LPG is produced, is one where the metallic components are impregnated or ion-exchanged upon a crystalline aluminosilicate molecular sieve, a variety of which are commonly referred to in the art by the broad term "zeolites". For example, one such catalyst which exhibits the desired characteristics of stability and activity, is a composite of about 5.3% by weight of nickel and a synthetically-prepared faujasite which is distributed throughout a silica matrix. Other suitable zeolitic materials include mordenite, Type X or Type Y molecular sieves, as well as zeolitic material which is dispersed within an amorphous matrix of alumina, silica, or alumina-silica.

In view of the fact that hydrocracking reactions are principally exothermic in nature an increasing temperature gradient will be experienced as the charge stock and hydrogen traverse the catalyst. Therefore, in order to prevent too great a temperature rise in the hydrocracking reaction zones, it is contemplated that a quench stream, either normally liquid, or normally gaseous, may be introduced at one or more points in the hydrocracking reaction zone. The fresh feed charge stock, in admixture with hydrogen and desirably also with a 400°F.-plus normally liquid recycle stream, is introduced into the first hydro-

cracking reaction zone at a temperature such that the increasing temperature gradient is maintained at the desired, pre-determined level. The total product effluent is introduced, at substantially the same pressure as in the first reaction zone, into a hot separator from which the gasoline boiling range hydrocarbons are removed as a vaporous phase. Prior to entering the hot separator, the temperature of the first zone effluent is decreased, via heat-exchange to a level such that the vaporous fraction will contain a minimum of material boiling above the gasoline boiling range. The unconverted portion of the fresh feed charge stock is withdrawn from the hot separator as the liquid phase, and preferably recycled to combine with the fresh feed charge stock. The vaporous phase serves as the charge to the second hydrocracking reaction zone, wherein the same is subjected to conversion to liquefied petroleum gas. It is within the scope of the present invention to divert a portion of the effluent from the first hydrocracking reaction zone to a suitable separation system. This affords a measure of flexibility in that it permits recovery of gasoline boiling range material when fluctuations in marketing considerations so demand. The pressure imposed on the second hydrocracking reaction zone is suitably substantially the same as that at which the vaporous phase is withdrawn from the hot separator; however, the temperature will be increased to provide a higher severity operation. Again without a reduction in pressure, excepting that experienced from friction losses resulting from the flow of fluids through the system, the effluent from the second hydrocracking reaction zone is cooled to a temperature in the range of 60°F. to 140°F. and introduced into a cold separator.

A hydrogen-rich vaporous phase is withdrawn from the cold separator and preferably recycled, via compressive means, to combine with the fresh feed charge stock to the first hydrocracking zone. Make-up hydrogen, required to supplant that consumed within the overall process and "lost" solution, is preferably introduced into the hydrogen recycle line downstream of the compressive means. Pressure control over the entire system is facilitated by monitoring the pressure of the vaporous phase as it emanates from the cold separator. A normally liquid phase, containing unreacted gasoline boiling range hydrocarbons, pentanes, hexanes, and the desired propane/butane concentrate is withdrawn from the cold separator and introduced into a suitable separation system wherein the various streams are recovered. The unreacted gasoline boiling range hydrocarbons are, at least in part, preferably recycled to combine with the material being charged to the second reaction zone. In one embodiment of this invention, a portion of the unreacted gasoline boiling range hydrocarbons is admixed with the effluent from the first reaction zone prior to introducing the same into the hot separator.

In further describing the invention, reference will be made to the accompanying drawing which illustrates one embodiment thereof. It is not intended that the invention be limited to the illustrated embodiment in which miscellaneous appurtenances such as heaters, pumps, compressors, heat-exchangers, start-up lines, control valves, etc., have been eliminated. Such items are well within the purview of those possessing skill in the art, and are not essential to an understanding of this invention as hereinbefore described.

The drawing will be described in conjunction with a commercially-scaled unit designed to produce maximum quantities of a propane/butane concentrate from a blend of relatively heavy gas oils. Pertinent properties of this fresh feed charge stock are presented in the following Table I:

TABLE I
Gas Oil Charge Stock Properties

Gravity, °API	30.1
ASTM Distillation, °F.	
Initial Boiling Point	500
10%	640
30%	680
50%	710
70%	750
90%	840
End Boiling Point	1020
Sulfur, wt.%	0.93
Nitrogen, ppm.	600

The fresh feed charge stock is subjected to a hydrorefining technique utilizing a catalytic composite of an alumina-silica carrier material containing 37.0% by weight of silica, combined with 1.8% by weight of nickel and 16.0% by weight of molydbenum, calculated on an elemental basis. The reaction zone is maintained under an imposed pressure of about 2,000 psig., with a maximum catalyst bed temperature of about 850°F. The fresh feed charge rate is 4,500 barrels per day, the hydrogen concentration is about 6,500 scf/Bbl. and the liquid hourly space velocity is

0.70. Hydrogen consumption, within the hydrorefining system is about 770 scf/Bbl. or 1.32% by weight of the total fresh feed. The hydrorefining yields and product distribution are presented in the following Table II:

TABLE II
Hydrorefining Product Distribution and Yields

Component	Wt.%	Vol.%	Bbl/day
Ammonia	0.07	—	—
Hydrogen Sulfide	0.99	—	—
Methane	0.15	—	—
Ethane	0.25	—	—
Propane	0.49	0.85	38
Butanes	1.07	1.62	73
Pentanes	0.88	1.23	55
Hexanes	1.08	1.37	62
C_7—390°F	12.13	14.08	634
390°F.-plus	84.21	89.66	4035

It will be noted from the foregoing Table II that, although the principal reactions effected are desulfurization and denitrification, a significant quantity of hydrocracking is effected to produce lower-boiling hydrocarbons. The 111 Bbl./day of propane/butane concentrate will be added to the overall liquefied petroleum gas pool, while the heptane-390°F. naphtha fraction, in an amount of 634 Bbl./day, will be introduced into the second hydrocracking reaction zone. The 4,035 barrels per day of 390°F.-plus hydrocarbonaceous material constitutes the charge to the present two-stage process in line 1, as indicated on the accompanying drawing.

The charge in line 1 is admixed with about 2,400 barrels per day of a normally liquid recycle stream from line 2, the source of which is hereinafter set forth, resulting in a combined liquid feed ratio of about 1.6. Recycle hydrogen, in an amount of about 10,000 scf./Bbl is admixed via line 3, the total charge continuing through line 1 into hydrocracking reactor 4. Reactor 4 is maintained under an imposed pressure of about 2,100 psig., with a maximum catalyst bed temperature of about 750°F. The liquid hourly space velocity, based only upon the 4,035 barrels per day of fresh feed, is 0.81. The product effluent is withdrawn by way of line 5 and, following heat-exchange to reduce its temperature to a level of about 400°F., is introduced into hot separator 6 at a pressure of about 2,075 psig. The product yield and distribution from hydrocracking reactor 4 is given in the following Table III:

TABLE III
Reactor 4 Product Distribution and Yields

Component	Wt.%	Vol.%	Bbl./day
Methane	—	—	—
Ethane	0.11	—	—
Propane	2.59	4.20	169
Butanes	12.75	18.39	742
Pentanes	12.76	16.78	677
Hexanes	12.61	15.07	608
C_7—390°F.	60.80	66.26	2674

The yields presented in the foregoing Table III are exclusive of the 2,400 Bbl./day of 390°F.-plus material withdrawn from hot separator 6 as a normally liquid phase, and recycled via line 2 combined with the 4,035 Bbl./day of charge stock in line 1.

A principally vaporous phase is withdrawn from hot separator 6 by way of line 7, combined with unreacted naphtha in line 8 and the 634 Bbl./day of naphtha from the hydrorefining system (not illustrated in the drawing), the mixture continuing through line 7 into the second hydrocracking reaction zone 9. The charge enters reaction zone 9 at a pressure of about 2,050 psig, the maximum catalyst bed temperature being about 900°F. The liquid hourly space velocity is about 1.0, and the quantity of hydrogen is the same as in reactor 4, less that which was consumed by the reactions being effected therein.

The product effluent from reaction zone 9 is withdrawn by way of line 10 and introduced into cold separator 11 at a pressure of about 2,025 lbs. following heat-exchange and further cooling to reduce the temperature to a level of about 100°F. A hydrogen-rich recycle gaseous phase is withdrawn through line 3 and admixed with the charge stock in line 1, while a principally liquid phase, containing the propane/butane concentrate is withdrawn by way of line 12 and introduced into separation system 13. Ethane and lighter components are indicated as being withdrawn through line 14, the propane/butane concentrate through line 15, the pentane/hexane concentrate through line 16 and about 1,700 Bbl./day of normally liquid material by way of line 8 for recycle to combine with the vaporous phase in line 7.

Hydrogen consumption in reactor 9 is 1,560 scf./Bbl. of the total heptane-390°F. material being charged thereto. Since the combined liquid feed ratio is 1.5, the hydrogen consumption, based only on "fresh" heptane-390°F. feed, is about 937 scf./Bbl.

Total liquid yields are presented in the following Table IV:

TABLE IV

Total Product Yields, Bbl./day

Component	Pretreatment	Reactor 4	Reactor 9	Total
Propane	38	169	1237	1444
Butanes	73	742	1761	2576
Pentanes	55	677	1018	1750
Hexanes	62	608	410	1080
Total	228	2196	4426	6850

Liquefied Petroleum Gas is produced in a total amount of 4,020 Bbl./day, inclusive of the 111 Bbl./day derived from the hydrorefining reaction zone, or 89.3 vol.% of the original fresh feed of 4,500 Bbl./day.

WHAT WE CLAIM IS:—

1. A process for the production of liquefied petroleum gas which comprises the steps of:

(a) reacting a hydrocarbonaceous charge stock boiling above the gasoline boiling range and hydrogen in a first reaction zone at hydrocracking conditions selected to produce gasoline boiling range hydrocarbons;

(b) separating the resulting first reaction zone effluent in a first separation zone at substantially the same pressure as in the first reaction zone and at a temperature to provide a first vaporous phase containing gasoline boiling range hydrocarbons and a first liquid phase containing hydrocarbons boiling above the gasoline boiling range;

(c) reacting said first vaporous phase in a second reaction zone at hydrocracking conditions selected to convert normally liquid hydrocarbons to liquefied petroleum gas components;

(d) separating the resulting second reaction zone effluent in a second separation zone at substantially the same pressure as in the second reaction zone and a temperature in the range of 60°F. to 140°F. to provide a second vaporous phase and a second liquid phase; and,

(e) further separating said second liquid phase to provide a third liquid phase containing unreacted gasoline boiling range hydrocarbons and to recover said liquefied petroleum gas.

2. The process of Claim 1 further characterized in that at least a portion of said first liquid phase is recycled to said first reaction zone.

3. The process of Claim 1 or Claim 2 further characterized in that at least a portion of said third liquid phase is recycled to said second reaction zone.

4. The process of Claim 1 or Claim 2 further characterized in that at least a portion of said third liquid phase is recycled to said first separation zone.

5. The process of any of claims 1 to 4 further characterized in that said second vaporous phase is recycled to said first reaction zone to provide hydrogen for use therein.

6. The process of any one of Claims 1 to 5 further characterized in that said first and second reaction zones are catalytic, and contain a catalytic composite of a porous carrier material and at least one metallic component selected from Groups VI-B and VIII of the Periodic Table.

7. The process of Claim 6 further characterized in that the catalyst disposed in said first reaction zone is a composite of an amorphous carrier material, a Group VI-B metal component and a Group VIII metal component.

8. The process of Claim 6 or Claim 7 further characterized in that the catalyst disposed in said second reaction zone is a composite of a zeolitic carrier material and a Group VIII metal component.

9. A process for the production of liquefied petroleum gas substantially as hereinbefore described with reference to the accompanying drawing.

10. Liquefied petroleum gas when produced by the process of any of claims 1 to 9.

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1391649 COMPLETE SPECIFICATION

1 SHEET *This drawing is a reproduction of the Original on a reduced scale*